Supporting Information

Beyond the Melting Point Annealing of Poly (vinylidene fluoride) for Enhanced Piezoelectric Performance

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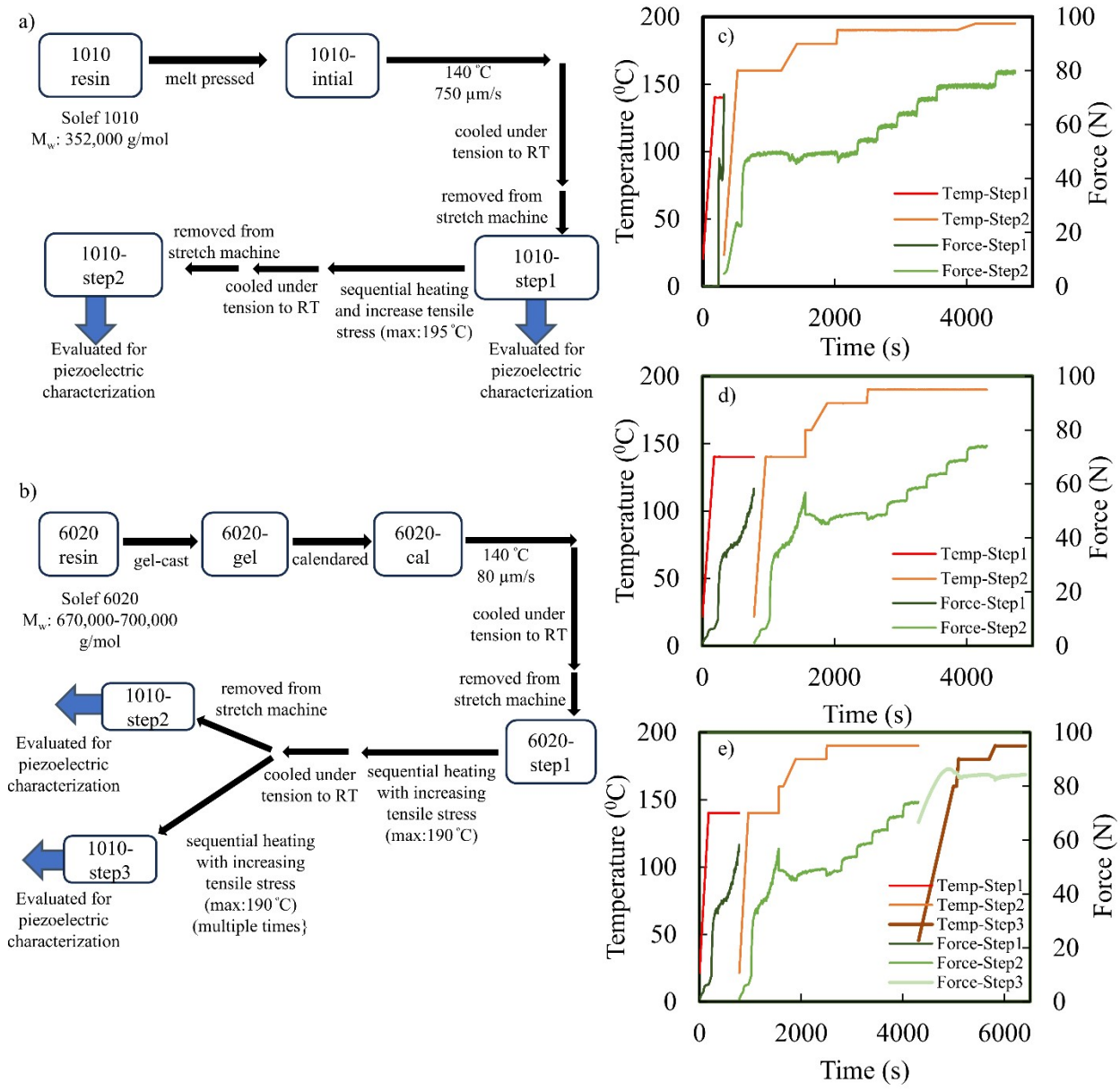

Fig S1. Schematic of the a) 1010 process and the b) 6020 process. Example Force/Temperature curve of the entire process for c) 1010-step1,2 films; d) 6020-step1,2 e) 6020-step1,2,3 films.

S1.1 Polarized FTIR in the ATR or Transmission Mode

However, due to the anticipated chain alignment in our films, polarized measurements of the film would be more useful. Differences in polarized IR light interactions with directional molecular vibrations have been used to measure the crystal and amorphous chain alignment of PVDF films(1–4) and as well as characterize alignment in other polymers(5–7). Furthermore, even unpolarized light will split into a Transverse Electronic (TE) and Transverse Magnetic (TM) upon total internal reflection. These TE and TM reflections will have different mode volume

interactions, leading to different signals depending on orientation for anisotropic films regardless if the IR light was polarized(8). While not a concern for isotropic films, in our anticipated highly stretched anisotropic films, the issue of MD orientation is more of a concern.
To control this effect, we polarize the incoming IR light, such that the only ATR-FTIR light interacting with the sample is the TE orientation, similar to previous reports(7,8). As shown in Figure S2, equivalent ⊥ and ∥ molecular-IR interactions to polarized transmission mode IR can be obtained by rotating the film with respect to the beam direction/electric field (TE).

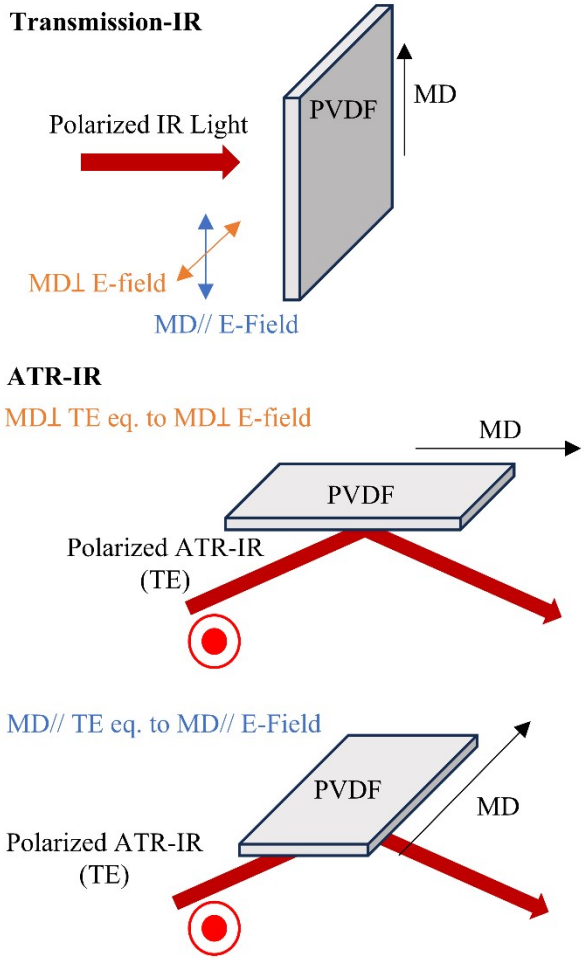

Fig. S2: Schematical representation of Polarized Transmission IR and Polarized ATR-IR. Note similar MD-Light interactions between transmission and ATR can be achieved

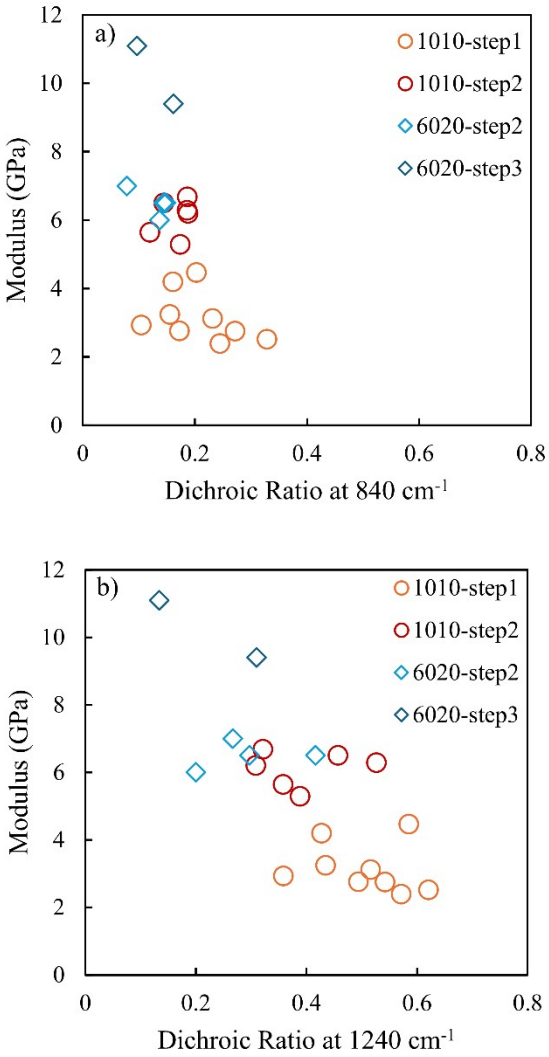

Figure S3: Comparison of Modulus with Dichroic Ratio at β peaks at a) 840 cm^{-1} and b) 1240 cm^{-1}

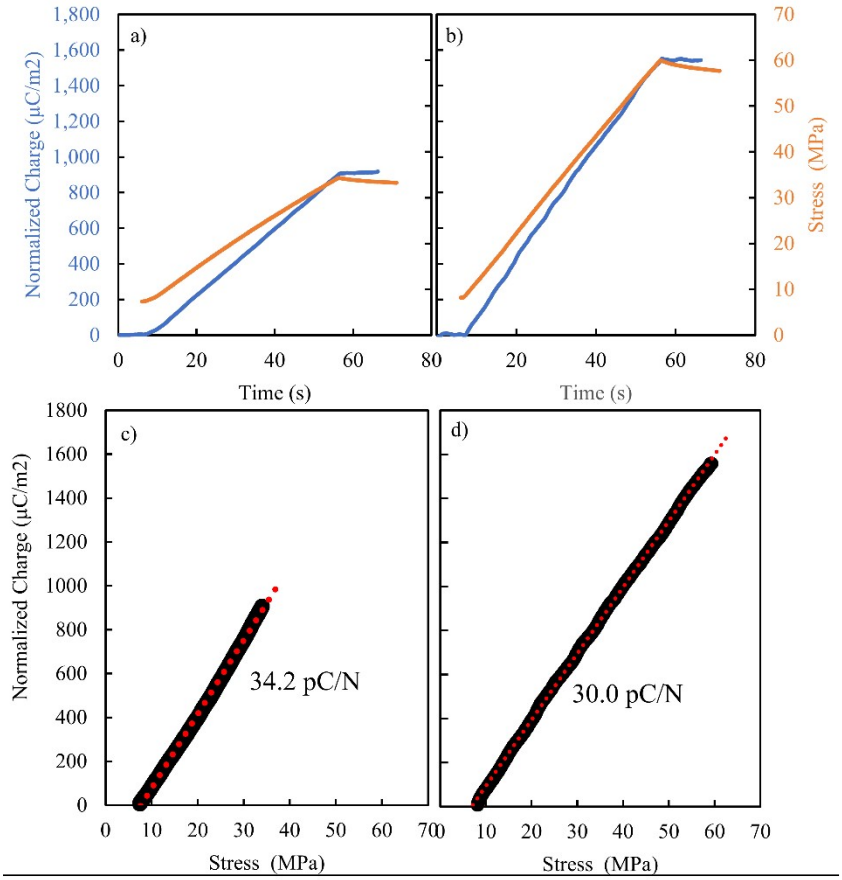

Fig. S4: Example stress and normalized charge curve for a) 1010-step1 film b) 6020-step2 film. Example of how the slope of the normalized charge compared to stress is used to compute the d_{31} of the same of c)1010-step1 and d) 6020-step2 film

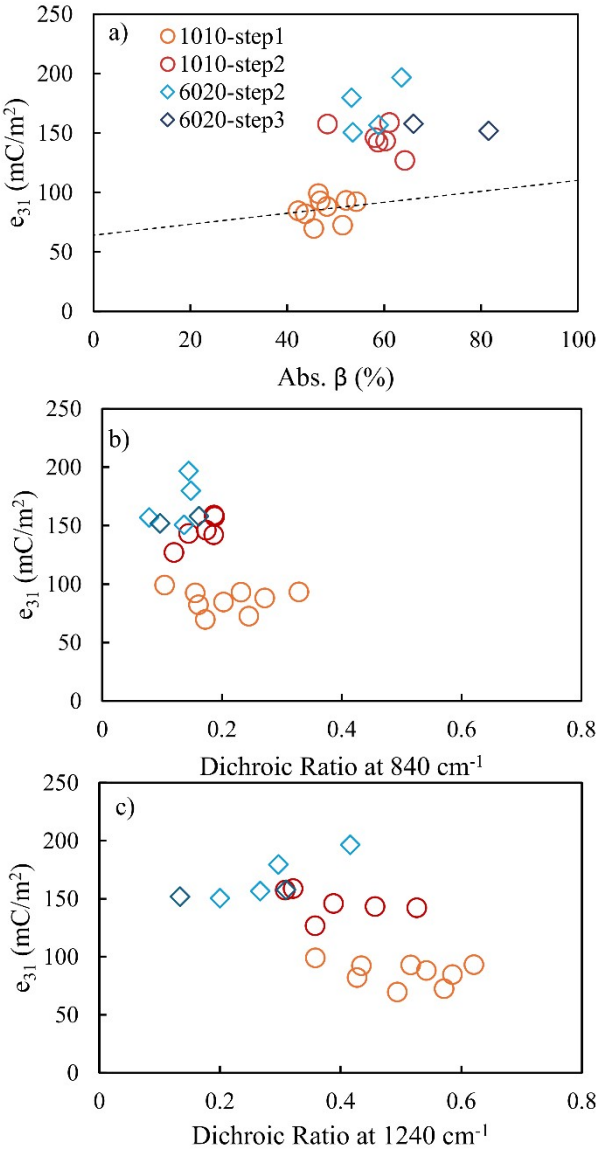

Fig. S5: Comparison of e_{31} with respect to a) abs. β content and Dichroic Ratios at b) 840 cm^{-1} and c) 1240cm^{-1}.

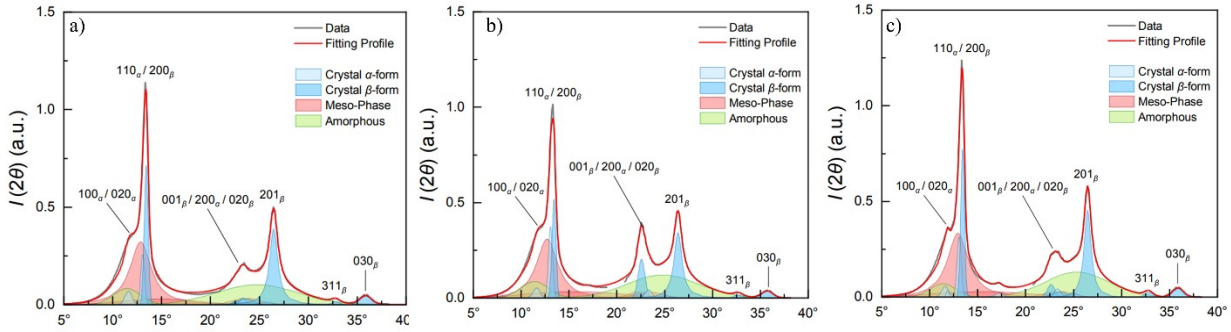

Fig. S6: WAXS analysis of a) 1010-step1, b) 1010-step2, c) 6020-step2 films.

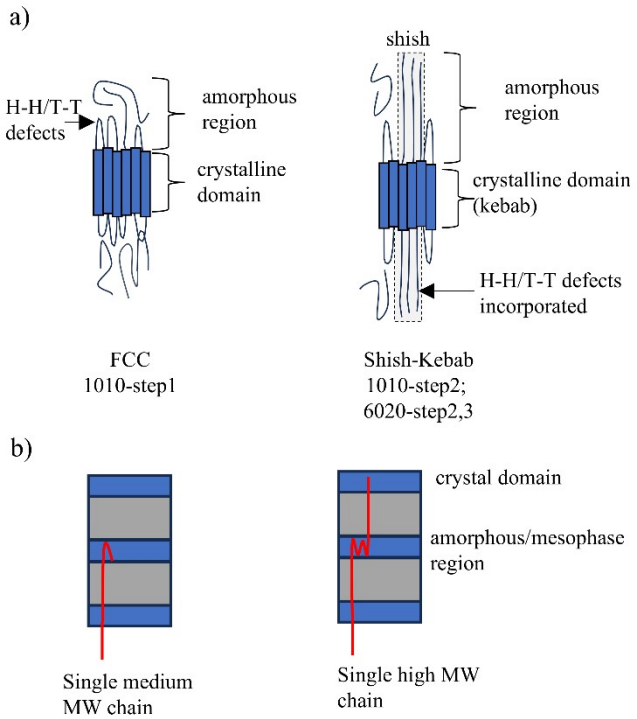

Fig. S7: a.) Schematical depiction of the difference between FCC crystal/amorphous (1010-step1) and Shish-Kebab crystals (1010-step2; 6020-step2,3). Note the changes at the crystal-amorphous interface are different between FCC & Shish-Kebab. b.) A potential difference between the shorter chain 1010-step2 films and longer chain 6020-step2,3 films. Due to the longer chain length for 6020, a single chain may extend into multiple different crystals and kebabs

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